Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting information

Sustainable Food Packaging Using Modified SiO_2 Nanofillers in Biodegradable Polymers

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Scanning electron microscopy (SEM)

SEM was performed to observe microstructural features of composite films, which were prepared for the gas permeability test. Composite films were immersed in liquid nitrogen for 30 minutes, then broken manually by bending. High-vacuum secondary electron imaging of the fractured surface was performed using an Aprea VS SEM (Thermo Scientific, the Netherlands) at an acceleration voltage of 1 kV.

Differential Scanning Calorimetry

The thermal behavior of the nanocomposites was measured using the differential scanning calorimeter (DSC) under nitrogen atmosphere. The samples of 8.5 ± 0.5 mg were heated from 20 to 190°C and kept under isothermal conditions at 190°C for 3 min to eliminate the thermal history. Then the samples were cooled to 20°C and finally were reheated to 190°C. The cooling and heating rate was 10°C·min^{-1}. The cooling and second heating curves were recorded. For each sample, the reported value is the average of three measurements. The crystallinity (χ_c) of the PHBV and PLLA phases was calculated by:

$$\chi_c\,(\%) = \left(\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times w_f}\right) \times 100\%$$

where ΔH_m is the melting enthalpy, ΔH_{cc} is the cold crystallization enthalpy, w_f belongs to the weight fraction of polymer and ΔH_m^0 is the melting enthalpy of completely crystallized polymer (100% crystalline). For PLLA ΔH_m^0 = 93 J/g[1] and for PHBV due to low content of HV the theoretical fusion enthalpy ΔH_m^0 is chosen as 146 J/g , which corresponds to 100% crystalline PHB [2].

Water uptake

To examine the water uptake, samples were dried for 72h, then immediately weighed (W_0) and immersed in 80 ml of MlliQ water at 23.1 ± 0.1 °C for 14 days. After every 24h, the samples were taken out from water, dried surface with tissue, and weighed (W_1) using an electronic semi-microbalance Sartorius R160P (Sartorius GmbH, Goettingen, Germany). For each sample the reported value is the average of five tests. The water absorption (Wa) of the samples was calculated with the following equation[3] :

$$Wa = \frac{W_1 - W_0}{W_0} \times 100\%$$

Biodegradation tests

In order to evaluate the biodegradation properties of the filler and nanocomposites, a four-stage research scheme was implemented in accordance with the general recommendations of EN 13432 standard, which provides guidelines for test selection and test parameter design. Therefore, for the purpose of this study only the (idealized) biodegradation test according to OECD 301B (modified Sturm test) was required. All biodegradation test were set up as aquatic aerobic biodegradation test. We used the mineral medium as recommended in 500 mL glass bottles (Shott) equipped with the fitting gas washing unit. Test volume was 400 mL plus 10 mL of an mixed bacteria inoculum plus the amount of reference or test substance which was equivalent to ca. 0.3 to 0.6 g carbon. The carbon content of the substances was determined by element analysis with the photo-oxidation principle. Inocula were either enriched sewage sludge (settled for four hours, supernatant decanted and residue with roughly 2-3 % dry solid matter used) for mesophilic test conditions or an elutriate from organic waste compost (by suspending active compost in warm tap water, removing stones and swimming particles and using the rest as it is) for thermophilic test conditions. Each test setup consisted of a blanc, a reference substance and any number of test substance, each of them in threefold replicates. In case of limited sample amounts, only twofold determinations were done.

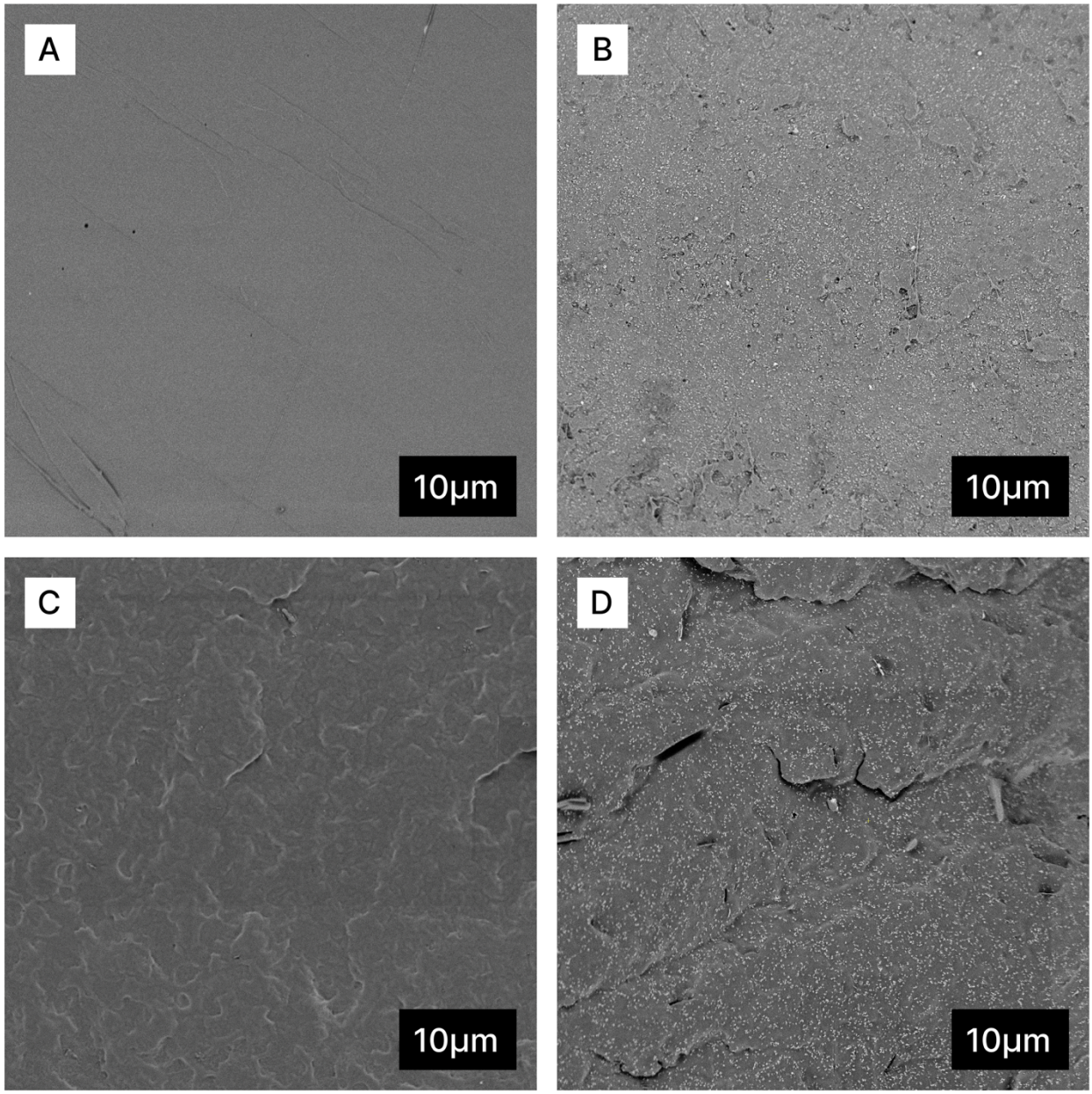

Figure S1. SEM micrographs of cryogenically fractured films of (A) PLLA, (B) PLLA/OLLA-g-SiO_2, (C) PHBV and (D) PHBV/OLLA-g-SiO_2.

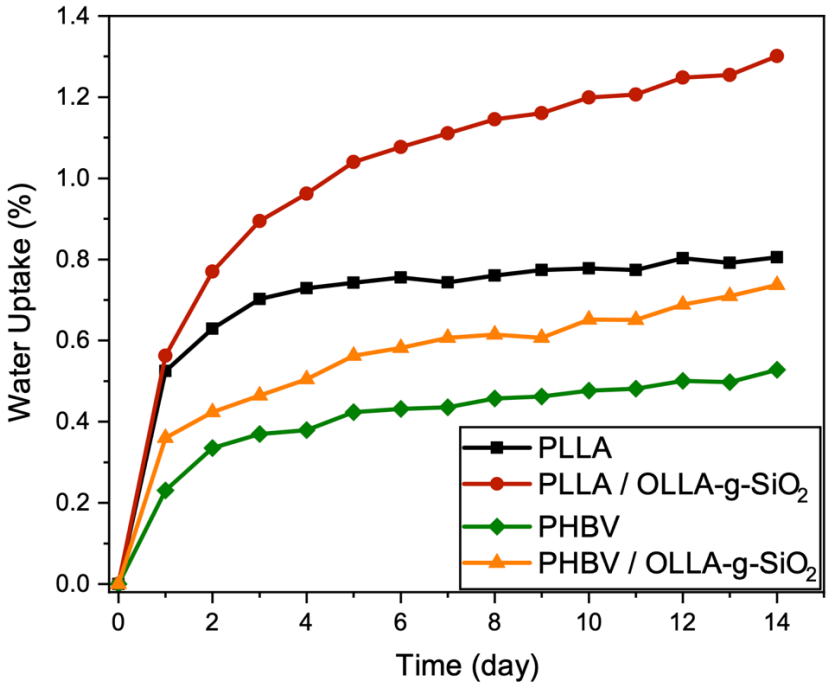

Figure S2. Water absorption profiles for PLLA, PLLA/OLLA-g- SiO_2, PHBV and PHBV/OLLA-g-SiO_2 at 23 °C.

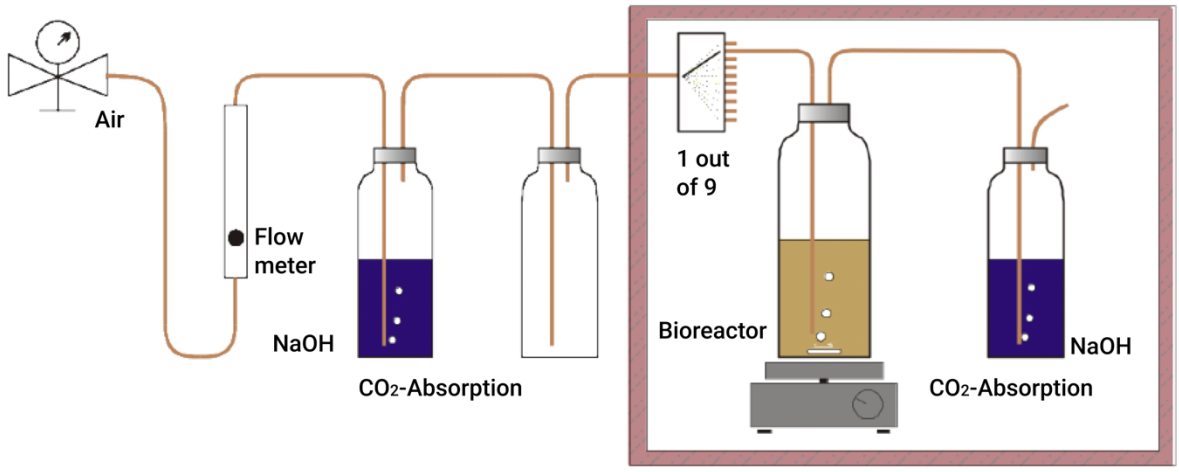

Figure S3: General setup of the biodegradation tests according to OECD 301B, the temperature of bioreactor was set to either 22°C or to 58°C.

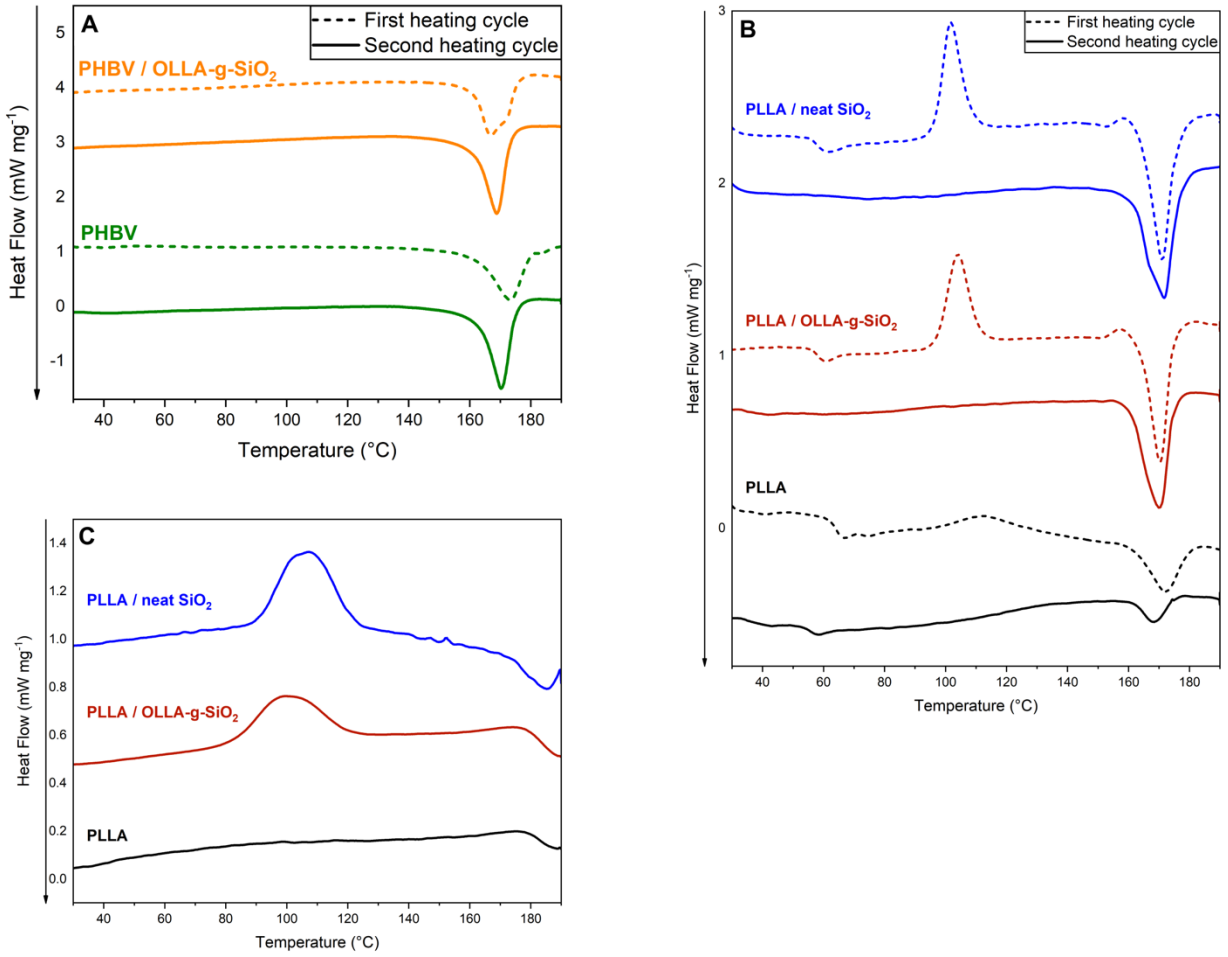

Figure S4. Differential scanning calorimetry (DSC) for PHBV and PHBV/OLLA-g- SiO_2 (A), PLLA, PLLA/OLLA-g-SiO_2 and PLLA/neat SiO_2 (B) and cooling cycle for PLLA, PLLA/OLLA-g-SiO_2 and PLLA/neat SiO_2 (C)

Table S1. Thermal characteristics of PLLA and PHBV and their nanocomposites.

Sample	w_f (%)	First heating cycle			Second heating cycle		
		T_{m1} (°C)	ΔH_{m1} (J/g)	χ_{c1} (%)	T_{m2} (°C)	ΔH_{m2} (J/g)	χ_{c2} (%)
PLLA	100	171.7 ± 0.6	5.8 ± 0.4	6.2	169.4 ± 0.7	7.3 ± 0.2	7.8
PLLA/ OLLA-g-SiO_2	95	171.9 ± 0.3	8.1 ± 1.7	9.2	171.4 ± 0.9	35.1 ± 0.9	39.7
PLLA/ SiO_2	95	171.4 ± 0.3	8.5 ± 0.9	9.7	171.6 ± 0.5	39.3 ± 3.2	44.5
PHBV	98.5	172.6 ± 0.7	75 ± 2.4	52.0	170.4 ± 0.5	88 ± 1.1	61.3
PHBV/ OLLA-g-SiO_2	93.6	170.6 ± 0.5	66 ± 2.5	48.3	171 ± 1.2	90 ± 1.3	66.1

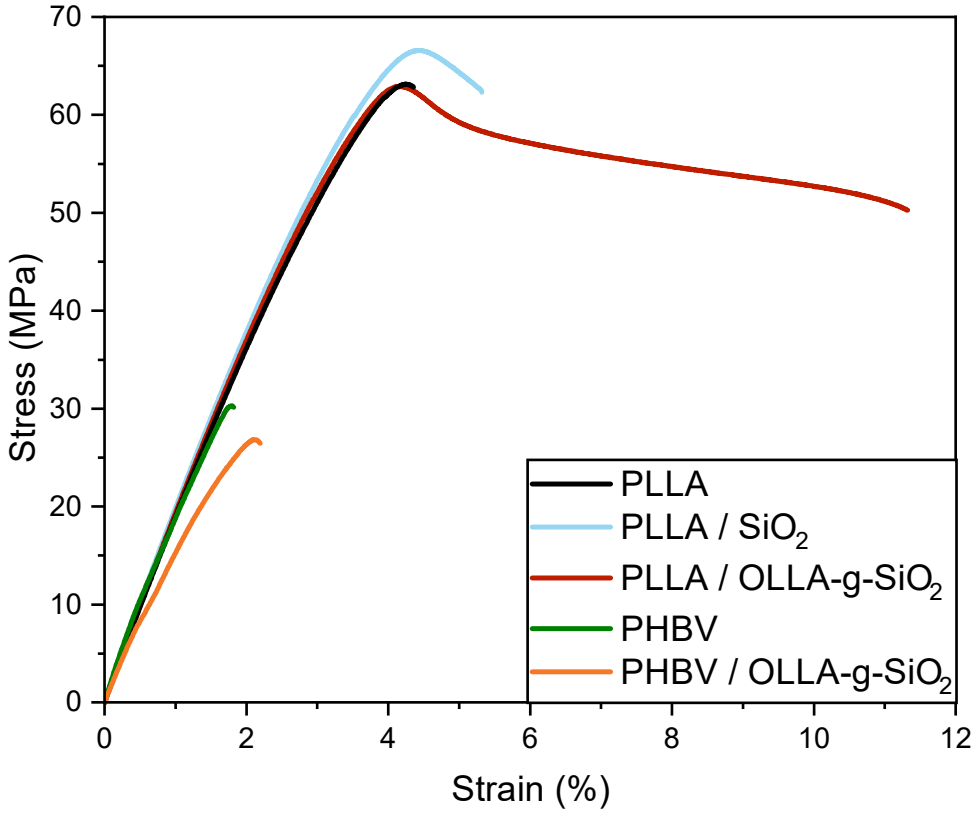

Figure S5. Stress-strain curves for PLLA, PLLA/SiO_2 PLLA/OLLA-g-SiO_2, PHBV and PHBV/OLLA-g- SiO_2

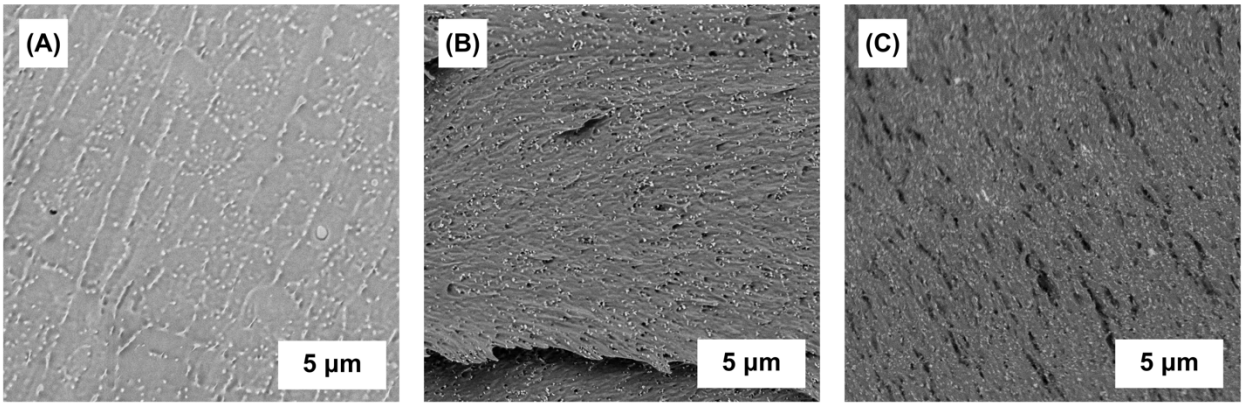

Figure S6. SEM micrographs of "dogbone" specimens after tensile tests of (A) PLLA, (B) PLLA/unmodified SiO_2, (C) PLLA/OLLA-g-SiO_2.

References

1 E. W. Fischer, H. J. Sterzel and G. Wegner, *Kolloid-Zeitschrift & Zeitschrift für Polymere*, 1973, **251**, 980–990.

2 P. J. Barham, A. Keller, E. L. Otun and P. A. Holmes, *J Mater Sci*, 1984, **19**, 2781–2794.

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